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12 a. DISTRIBUTION / AVAILABILITY STATEMENT

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12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

We developed an *in situ* IR transmission electrochemical cell, which was initially used to study lithium intercalation in a phospho-olivine Li_xFePO_4 cathode. We had previously characterized vibrational spectrum of this material as part of a preliminary study. The transition between $LiFePO_4$ and $FePO_4$ could easily be followed in the *in situ* spectra.

An industrially available coin cell was modified to facilitate routine *in situ* Raman measurements of lithium batteries. Available *in situ* Raman cells are usually designed to optimize optical throughput, resulting in cell geometries significantly different from those used in "normal" electrochemical investigations. The charge/discharge curves of our cell were very similar to those of unmodified coin cells. This cell was used to study lithium intercalation in a lithium vanadium pentoxide cathode.

We studied lithium intercalation reactions in a series of phosphate-based electrode materials including $LiSn_2(PO_4)_3$, $Sn_3(PO_4)_2$, the monoclinic and rhombohedral phases of $Li_3V_2(PO_4)_3$, $LiTi_2(PO_4)_3$ and $Li_x(Mn_yFe_{1-y})PO_4$ ($0 < x \le 1$). After identifying those phosphate ion modes most sensitive to changes in the vibrational potential energy environment and lithium "cage" modes, we were able to draw important conclusions about various mechanisms (e.g. two-phase mechanisms, alloying mechanisms) based on observed local structural changes accompanying lithium insertion/removal.

14. SUBJECT TERMS
in situ IR transmission spectroscopy, *in situ* Raman spectroscopy, intercalation electrodes, lithium batteries

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1. Forward

In this project, we have demonstrated the power of *in situ* vibrational spectroscopy to study lithium insertion/extraction reactions in a variety of intercalation electrodes. Vibrational spectroscopic measurements are very sensitive to subtle structural changes in the electrode materials that accompany either a global change in phase or the onset of disordering in a sublattice. In the various electrode materials of interest in this study, we were able to distinguish between mechanisms of lithium insertion/removal reactions (e.g. two-phase behavior, alloying, topotactic substitution) through the use of spectroscopic techniques. The sensitivity of vibrational spectroscopy to very small structural changes enabled us to observe reversibility, or in some cases the lack of reversibility, at the molecular level.

2. Table of Contents—Summary of Results, Sec. 5

3. List of Illustrations and Tables

Figure 1. Schematic diagram of *in situ* IR transmission electrochemical cell.

Figure 2. IR and Raman bands in the ν_1 and ν_3 PO$_4$ stretching region of pure $FePO_4$ and pure $LiFePO_4$ with *in situ* IR transmission spectra of the ν_2 and ν_4 PO$_4$ bending region.

Figure 3. Schematic diagram of *in situ* Raman electrochemical cell.

Figure 4. Comparison of electrochemical performance of *in situ* cell and unmodified coin cell with *in situ* spectra of lithium vanadium pentoxide during discharge.

4. Statement of Problem Studied

The goals of this project were to develop *in situ* infrared transmission spectroscopic techniques and apply these to study local structural changes accompanying lithium insertion/extraction reactions in a family of phosphate-based intercalation electrode materials. We elected to study the electrode materials Li_xFePO_4, $LiSn_2(PO_4)_3$, $Sn_3(PO_4)_2$, the monoclinic and rhombohedral phases of $Li_3V_2(PO_4)_3$, $Li_3V_2(PO_4)_3$, $LiTi_2(PO_4)_3$ and $Li_x(Mn_yFe_{1-y})PO_4$ ($0 < x \leq 1$). Although the original emphasis was on *in situ* infrared transmission spectroscopy, we found it useful to modify a commercially available coin cell to facilitate routine *in situ* Raman measurements of

lithium batteries. In many of these studies, the *in situ* data were combined with data obtained from *ex situ* studies.

For each electrode material, it was necessary to develop complete vibrational assignments and, more importantly, identify those modes whose frequencies and intensities are most sensitive to changes in the lithium content of electrode materials during cycling. It was also important to be able to quantify changes in lithium content in order to correlate points on the charge/discharge curve with observed changes in the vibrational modes. In most cases, the spectroscopic measurements were complemented by electrochemical, x-ray diffraction and thermal (DSC) studies.

5. Summary of the most important results

(a) Lithium intercalation studies of Li_xFePO_4.

The cathode material Li_xFePO_4 ($0 < x < 1$) was studied as a function of lithium-ion content using FTIR and Raman spectroscopy to provide background data for the planned *in situ* spectroscopic studies. The lithium content was varied by chemical delithiation and sample homogeneity was confirmed with an electron microprobe. This work yielded a number of interesting and significant results and conclusions.

i. The frequencies and intensities of a number of intramolecular PO_4^{3-} vibrations were shown to be sensitive to changes in lithium content. Coordination of the lithium ions with the oxygen atoms of the phosphate groups causes a redistribution of electron density in the P-O bonds, which changes the effective force constants (frequencies), dipole moment derivatives (IR intensities) and polarizability derivatives (Raman intensities). The electronic redistribution is also affected by the oxidation of the Fe^{2+} ions to Fe^{3+}.

ii. The morphology and particle size distribution of Li_xFePO_4 was explored with an electron microprobe. The sample was relatively homogeneous with respect to iron and phosphorous, and was primarily composed of larger particles (10-20 μm diameter) and smaller-sized particles (~1 μm diameter).

iii. The IR and Raman spectra clearly supported a two-phase model delithiation of delithiation of $LiFePO_4$, with a layer of $FePO_4$ forming around each $LiFePO_4$ particle as lithium ions are extracted. This picture is consistent with several reported structural studies.[1,2]

iv. The differences in the optical penetration depth for IR and Raman measurements yielded information concerning the delithiation process in the particles on two different spatial scales. The Raman spectra probe a region close to the surface because the optical skin effect sharply limits the penetration of the excitation laser beam into the particle, while the IR beam samples the entire particle.

This work was published as:

Burba, C. M.; Frech, R. " A Raman and FTIR Spectroscopic Study of Li_xFePO_4 ($0 \leq x \leq 1$)", *J. Electrochem. Soc.* **2004,** *151(7)*, A1032-A1038.

(b) In *situ* infrared transmission studies of lithium rechargeable batteries

During this project, we developed an electrochemical cell that would allow us to measure *in situ* IR transmission spectra. The cell design is illustrated in Figure 1.
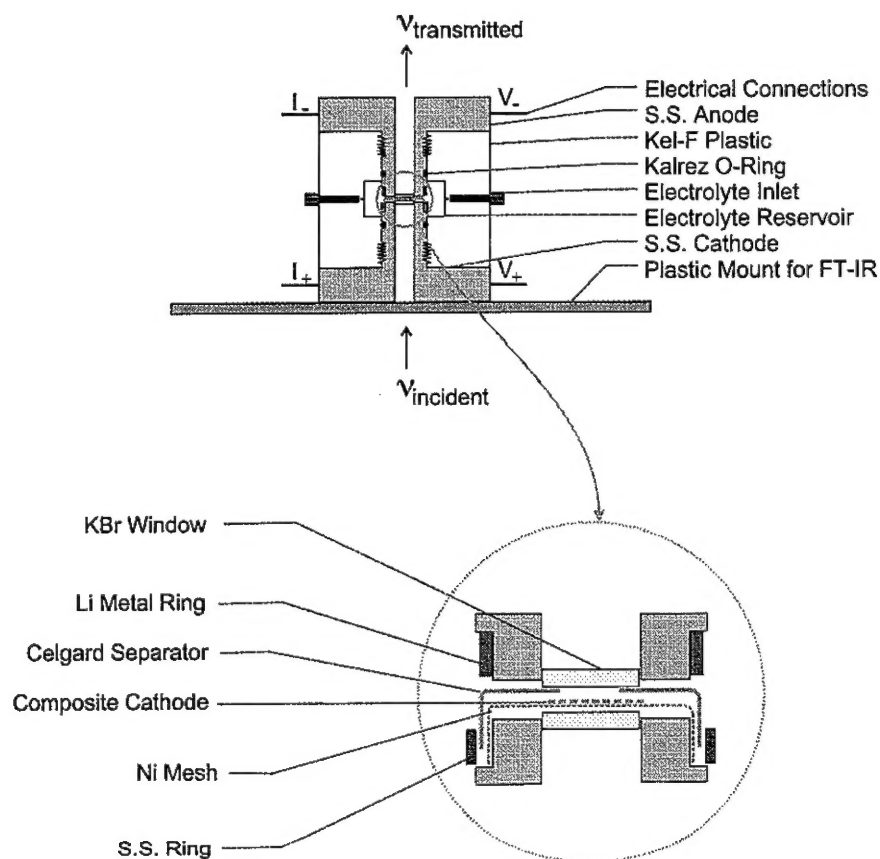
Figure 1. Schematic diagram of *in situ* IR transmission electrochemical cell.

With this cell, we studied the electrochemical insertion of lithium into phospho-olivine $FePO_4$ because of our previous experience with this system.[3] The spectroelectrochemical cell contained orthorhombic $FePO_4$ as the cathode (70% active material, 25% conductive carbon, 5% PVDF binder), a lithium anode, and an electrolyte of 1M $LiPF_6$ in a 1:1 mixture of ethylene carbonate and diethyl carbonate. *In situ* spectra and corresponding spectra of the pure end member components $FePO_4$ and $LiFePO_4$ are shown in Figure 2.
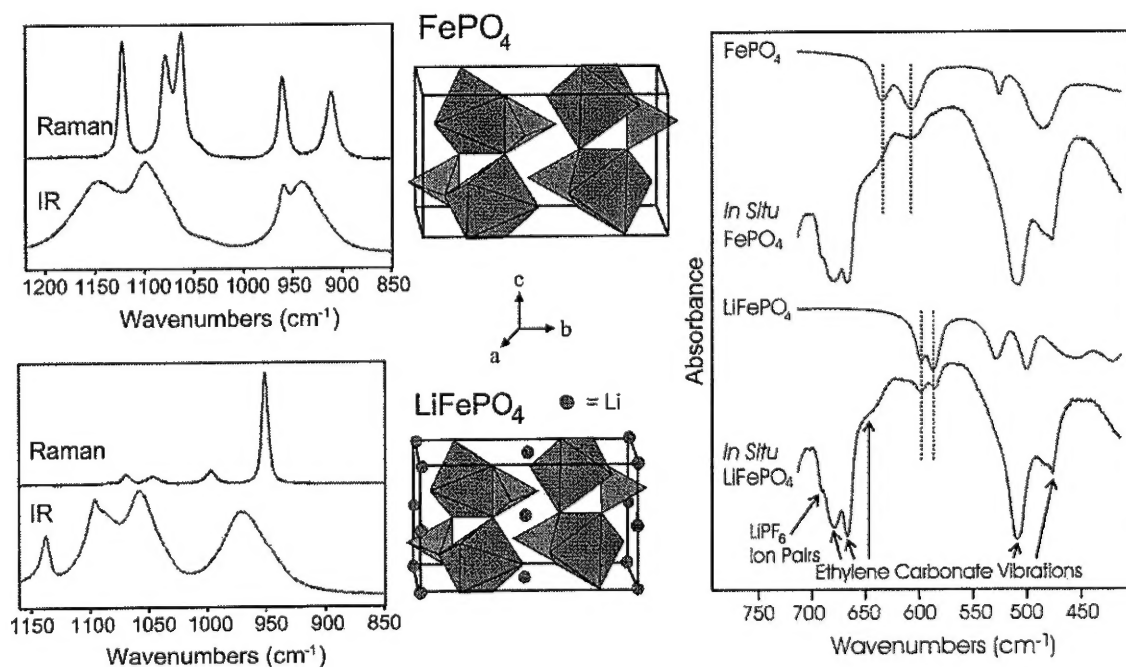
Figure 2. IR and Raman bands in the ν_1 and ν_3 PO_4 stretching region of pure $FePO_4$ and pure $LiFePO_4$ are shown in the left side to illustrate the striking difference in the vibrational potential energy environment of the two compounds. *In situ* IR transmission spectra of the ν_2 and ν_4 PO_4 bending region are shown on the right side.

Bands belonging to the electrolyte and the antisymmetric PO_4^{3-} bending vibrations (ν_4) of the cathode are easily observed in the spectra. The ν_4 modes are very sensitive to the presence of Li^+ ions and the oxidation state of the iron atoms. Therefore, these vibrations are used to monitor the insertion of Li^+ ions into $FePO_4$. Discharging the cells produces spectral changes that are consistent with the formation of $LiFePO_4$. The electrolyte bands are not affected when the cell is discharged.

These experiments demonstrate the usefulness of *in situ* transmission FT-IR spectroscopy in investigating fundamental reactions that occur during electrode cycling in lithium batteries. Sustained cycling of the cells caused lithium plating over the windows. Using an intercalation anode such as graphite would alleviate this problem.

This work was published as:

Burba, C. M.; Frech, R. "*In Situ* Transmission FTIR Spectroelectrochemistry: A New Technique for Studying Lithium Batteries", Electrochim. Acta **2006,** *52,* 780-785.

(c) *In situ* Raman spectroscopic studies of lithium rechargeable batteries

It is desirable to perform *in situ* Raman spectroscopic measurements of lithium insertion/removal reactions in intercalation electrodes without the need to construct highly specialized *in situ* Raman spectroelectrochemical cells. Therefore we modified an industrially available coin cell to facilitate routine *in situ* Raman spectroelectrochemical studies of rechargeable lithium batteries. This was accomplished by drilling a 2 mm diameter hole into the coin cell casing prior to cell assembly. After the coin cell was crimped closed, an optically transparent sapphire window (13 mm × 1 mm) was attached over the hole, pressed against the coin cell with a C-clamp and affixed in place with an epoxy resin. A diagram of the cell is illustrated in Figure 3.
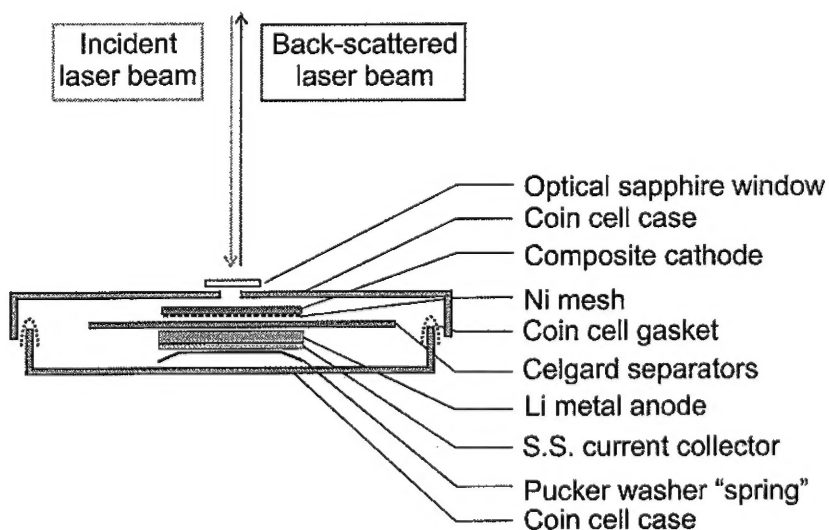

Figure 3. Schematic diagram of *in situ* Raman electrochemical cell.

To test this design, *in situ* Raman spectra were measured using an $Li|LiPF_6\text{-}EC\text{-}DEC|Li_xV_2O_5$ spectroelectrochemical cell. On the left side of Figure 4, the charging curve of a normal coin cell is compared with the cell modified as an *in situ* cell. The two curves are in reasonable agreement. The discharge capacities of the *in situ* cell followed the same trend as the normal cells, although the capacities were somewhat lower. This is probably due to inefficient usage of the electrode material covering the optical window. On the right side are *in situ* Raman spectra in which the various phases of $Li_xV_2O_5$ can be identified. These data were and

compared with analogous Raman spectra obtained during previous spectroscopic studies of various $Li_xV_2O_5$ phases.[4] Throughout all of these V_2O_5 studies, the electrochemical cycling performance of the *in situ* cells was very similar to the unmodified coin cells. These important observations provide a degree of confidence in results obtained from our *in situ* studies.
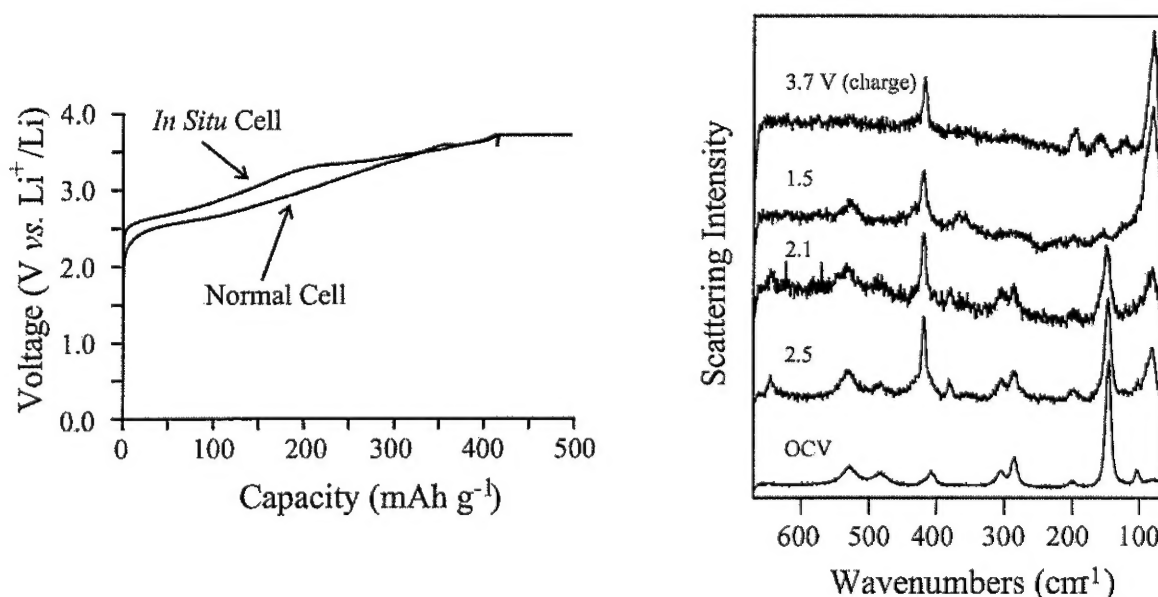

Figure 4. Comparison of electrochemical performance of *in situ* cell and unmodified coin cell (left figure). *In situ* spectra of lithium vanadium pentoxide during discharge (right figure).

This work was published as:
Burba, C. M.; Frech, R., "Modified Coin Cells for *In Situ* Raman Spectroelectrochemical Measurements of Rechargeable Lithium Batteries", *Appl. Spec.* **2006,** 60(5), 490-493.

(d) Ionic association in solutions of LiPF$_6$

In our development of *in situ* infrared transmission techniques, we used a variety of electrolytes containing dissolved LiPF$_6$. Ionic association in nonaqueous electrolytes containing LiPF$_6$ was investigated with infrared transmission spectroscopy. The spectral intensity of the nondegenerate ν_1 mode of the PF$_6^-$ anion was found to be sensitive to ion pairing through an unusual mechanism. The ν_1 mode of an isolated PF$_6^-$ anion is only Raman-active. However, coordination of Li$^+$ ions with PF$_6^-$ destroys the octahedral symmetry of the anion and results in ν_1 becoming simultaneously IR- and Raman-active. When the dielectric constant of the solvent is increased, the IR-intensity of the ν_1 band decreases because ion pairing is not favored in high dielectric solvents.

The significance of this work lies in the fact that LiPF$_6$-based electrolytes are often used in rechargeable lithium cells. It is important to recognize ion-pairing effects and not mistake these for products of electrolyte degradation.

This work was published as:
Burba, C. M.; Frech, R. "Spectroscopic Measurements of Ionic Association in Solutions of LiPF$_6$", *J. Phys. Chem. B* **2005,** *109*, 15161-15164.

(e) The first discharge of Li-Sn-PO$_4$

The first discharge of crystalline $LiSn_2(PO_4)_3$ and $Sn_3(PO_4)_2$ was investigated with infrared spectroscopy, XRD, DSC, and impedance spectroscopy. In the original compounds, PO_4^{3-} intramolecular vibrations and lattice modes were easily recognized in the infrared spectra [5] and were analyzed using factor group correlation methods. There are several results and conclusions to be noted.

i. The spectroscopic data throughout the discharge process may be explained by an alloying model.[6] Prior to discharging, both compounds had a rich vibrational structure in the mid- and far-IR; however, discharging to 1.00V completely destroyed this structure. The resulting mid- and far-IR spectra are consistent with the formation of highly disordered Li_3PO_4. Inserting lithium ions into $LiSn_2(PO_4)_3$ and $Sn_3(PO_4)_2$ destroyed the translational symmetry of these crystalline compounds and produced an inorganic matrix consisting primarily of disordered Li_3PO_4. Below 1.00 V, the Li_3PO_4 bands were not significantly affected by lithium insertion, which indicated that lithium ions alloy with tin at these voltages and did not react further with the inorganic matrix.

ii. Species originating in the SEI layer were observed in this study. Bands assigned to CO_3^{2-} species appeared rather suddenly in the mid-IR spectra of $LiSn_2(PO_4)_3$ and $Sn_3(PO_4)_2$. Simultaneously, peaks appeared in the differential capacity curves at voltages roughly corresponding to the formation of metallic tin. These CO_3^{2-} bands were assigned to the products of an electrolyte decomposition reaction catalyzed by the metallic tin that forms in these electrodes. Further, DSC measurements of the compounds as a function of voltage revealed the formation of thermally irreversible endothermic and exothermic peaks that are probably related to the carbonate species.

iii. The conductivity of $LiSn_2(PO_4)_3$ and $Sn_3(PO_4)_2$ samples dramatically increased when the electrodes were discharged to 0.01 V, consistent with the formation of Sn and Li-Sn alloy domains. Furthermore, XRD measurements confirmed the complete destruction of the host material's crystallinity, consistent with the spectroscopic data as described above.

This work was published as:

Burba, C. M.; Frech, R. "Electrochemical, Spectroscopic, and Thermal Investigations of $LiSn_2(PO_4)_3$ and $Sn_3(PO_4)_2$ Anodes During the First Discharge", *J. Electrochem. Soc. 152(6)*, **2005**, A1233-A1240.

(f) The monoclinic and rhombohedral phases of $Li_3V_2(PO_4)_3$.

Here our work focused on the value of powder XRD and wavelength dispersive spectrometry using an electron microprobe to augment vibrational spectroscopic analyses.[7] Studies characterizing the particle sizes of A- and B-$Li_3V_2(PO_4)_3$ [8]using an electron microprobe revealed that the experimentally measured particles sizes were much larger than the average crystallite domain sizes estimated from the XRD data. This is probably because the larger particles were aggregates of the smaller crystallites. Furthermore, two distinct size domains were detected in B-$Li_3V_2(PO_4)_3$. The smaller particles of B-$Li_3V_2(PO_4)_3$ were approximately the same size as those found in A-$Li_3V_2(PO_4)_3$. However, B-$Li_3V_2(PO_4)_3$ also contained much larger domains. Magnification of these regions showed that they are actually dense clusters of the smaller particles.

We found that the Raman band intensities were very weak, consequently Raman spectroscopy could not be used to investigate lithium intercalation in A- and B-$Li_xV_2(PO_4)_3$ cathodes. These weak intensities may be due to a thin disordered layer on the surface of the particles. Since the samples were darkly colored, the excitation laser beam suffered a severe optical skin effect and could only penetrate a very small distance into the particles. Thus, the laser predominantly sampled the surface of the particles, similar to the phenomenon seen in the study of Li_xFePO_4 reported in Section (a) of this report.

Our studies showed that the PO_4^{3-} intramolecular vibrations, [9] particularly the bending modes, were very sensitive to the extraction of Li^+ ions in A-$Li_3V_2(PO_4)_3$. Changes in the frequencies and intensities of the PO_4^{3-} bands as the cathodes are cycled are due to subtle changes in the Li^+ ion coordination number and the Li-O and V-O bond distances. Infrared spectra recorded throughout the solid solution regime are essentially a superposition of the D-$Li_{0.9}V_2(PO_4)_3$ and D-$Li_{2.1}V_2(PO_4)_3$ spectra with the relative intensities of the bands governed by the site occupancy of the Li^+ ions. The infrared spectrum of the fully discharged sample matched that of the pristine cathode, highlighting the excellent reversibility of this material. Pronounced band broadening observed in the infrared spectrum of A-$Li_xV_2(PO_4)_3$ with delithiation suggests that the PO_4^{3-} anions become locally disordered even though the global structure of the compound is retained.[10]

This work was published as:

Burba; C. M.; Frech, R. "Vibrational Spectroscopic Studies of Monoclinic and Rhombohedral $Li_3V_2(PO_4)_3$", *Solid State Ionics,* **2007**, 177, 3445-3454.

(g) Electrochemical insertion reactions in $LiTi_2(PO_4)_3$ cathodes.

We used vibrational spectroscopy to study electrochemical insertion of Li^+ into $LiTi_2(PO_4)_3$. In general, the PO_4^{3-} bending modes are much more sensitive to the insertion of Li^+ ions than the stretching modes. This was particularly evident for the ν_4 modes in the infrared spectrum and, to a lesser extent, the ν_2 modes in the Raman spectrum. Phosphate bending modes appear to be less localized than the stretching vibrations; thus, they are more susceptible to small structural changes in the unit cell. The frequencies of the vibrational modes did not depend on the concentration of the Li^+ ions in this cathode material. Instead, $Li_3Ti_2(PO_4)_3$ bands appeared and increased in intensity at the expense of $LiTi_2(PO_4)_3$ bands. This type of behavior is indicative of a two-phase mechanism for the electrochemical insertion of Li^+ into $LiTi_2(PO_4)_3$.[11] Lithium ion cage modes were also identified in the infrared spectrum of $Li_3Ti_2(PO_4)_3$. According to crystallographic data, all three Li^+ ions reside in M(3) and M'(3) sub-sites of the larger M(2) cavities. Analogous bands did not appear in the Raman spectrum of $Li_3Ti_2(PO_4)_3$, even though the Li^+ ion cage modes are Raman active, because these vibrations typically have small polarizability derivatives. Hence, the Li^+ ion cage modes usually do not produce measurable Raman intensities.

This work was published as:

Burba, C. M.; Frech, R. "Vibrational Spectroscopic Study of Lithium Intercalation into $LiTi_2(PO_4)_3$", *Solid State Ionics*, **2006**, *177(17-18)*, 1489-1494.

(h) Local structure in the cathode materials $LiFePO_4$, $NaFePO_4$, and $FePO_4$.

Vibrational spectroscopy was utilized to investigate the local structure of $LiFePO_4$, $NaFePO_4$, and $FePO_4$. The factor group splitting of the intramolecular PO_4^{3-} vibrations was between 10 and 20 cm^{-1} less for $NaFePO_4$ than for $LiFePO_4$. This is because Li^+ ions have a higher charge density than Na^+ ions and can form stronger coordinative bonds with the PO_4^{3-} anions. Thus, the internal modes were more perturbed in $LiFePO_4$ and exhibited larger factor group splitting effects. The similarity of the factor group multiplets for both $LiFePO_4$ and $NaFePO_4$, particularly the PO_4^{3-} bending modes, strongly suggested that the 506 and 470 cm^{-1} bands of $LiFePO_4$ consist almost entirely of lithium translatory motion. There were marked differences between the vibrational spectrum of $FePO_4$ and those of $LiMPO_4$ (M = Mn, Fe, Co, or Ni) or $NaFePO_4$. The interaction of the monovalent cations with the oxygen atoms of the phosphate groups, affected the frequencies and intensities of the intramolecular PO_4^{3-} modes, in a manner that is absent in $FePO_4$.

This work was published as:

Burba, C. M.; Frech, R. "Vibrational Spectroscopic Investigation of Structurally-Related $LiFePO_4$, $NaFePO_4$, and $FePO_4$ Compounds", *Spectrochim. Acta A.* **2006**, 65(1), 44-50.

(i) Lithium intercalation in $Li-Mn-Fe-PO_4$ Cathodes

This work was a joint collaboration with the group headed by Prof. Josh Thomas of Uppsala University, Sweden. The Swedish group prepared a series of $Li_x(Mn_yFe_{1-y})PO_4$ ($0 < x \leq 1$) cathodes with y = 0, 0.5, and 1. We used infrared and Raman spectroscopy to demonstrate that the local structure of $Li(Mn_{0.5}Fe_{0.5})PO_4$ is very similar to that of $LiFePO_4$ and $LiMnPO_4$. In particular, the ν_1 and ν_3 bands exhibit two-mode behavior in the infrared spectra of $Li(Mn_yFe_{1-y})PO_4$,[12] whereas the frequencies of ν_4 and the Li^+ cage modes depend on the concentration of the Mn^{2+} ions. This is because ν_1 and ν_3 are more localized than either ν_4 or the Li^+ cage modes. The Raman spectra suggest that the carbon layer covering the surface of the $Li(Mn_{0.5}Fe_{0.5})PO_4$ particles is predominantly composed of sp^2-hybridized carbon atoms.[13] The vibrational modes of $Li(Mn_{0.5}Fe_{0.5})PO_4$ are sensitive to lithium extraction and may be used to investigate changes in the framework as the cathode is cycled. The lack of spectral changes during the Fe^{2+}/Fe^{3+} redox couple suggests that the PO_4^{3-} anions have similar local environments in $Li_{0.5}(Mn_{0.5}^{(II)}Fe_{0.5}^{(III)})PO_4$ and $Li(Mn_{0.5}^{(II)}Fe_{0.5}^{(II)})PO_4$. Two-phase behavior is confirmed during the Mn^{2+}/Mn^{3+} redox couple, and the infrared spectrum of $(Mn_{0.5}^{(III)}Fe_{0.5}^{(III)})PO_4$ is similar to

that of $FePO_4$. This is because both compounds contain PO_4^{3-} anions that are coordinated only to trivalent transition metal ions. However, the spectral data suggest that the PO_4^{3-} anions are much more disordered in $(Mn_{0.5}^{(III)}Fe_{0.5}^{(III)})PO_4$ compared to $FePO_4$. This is probably due to deformations of the MnO_6 octrahedra induced by the Jahn-Teller active Mn^{3+} ions in the $(Mn_{0.5}^{(III)}Fe_{0.5}^{(III)})PO_4$ structure.

This work has been submitted for publication as:
Burba; C. M.; Frech, R. "Local Structure in the Li-Ion Battery Cathode Material $Li_x(Mn_yFe_{1-y})PO_4$ for $0 < x < 1$ and $y = 0.0$, 0.5, and 1.0", *J. Power Sources*, submitted.

(j) Stretched PEO-based electrolytes.
We used polarized infrared transmission spectroscopy, complemented by wide-angle (WAXS) and small angle (SAXS) X-ray scattering to study the orientation effects in stretched films of polyethylene oxide, PEO, (5×10^6 da) containing lithium trifluoromethanesulfonate ($LiCF_3SO_3$). The films were prepared at (O:Li molar ratios of 20:1 and 10:1), and the samples were stretched by applying force until the film was elongated by roughly four-fold for the 20:1 film and two-fold for the 10:1 film. We observed that each spectrum of the stretched or unstretched films is a superposition of the pure PEO spectrum and the spectrum of the $P(EO)_3LiCF_3SO_3$ compound. The polarized spectra sharply discriminate between modes polarized along the elongation direction and modes polarized perpendicular to the elongation direction. It was possible to interpret these spectra using symmetry-based vibrational mode assignments for the appropriate helical groups.

This work has been accepted for publication as:
Burba; C. M.; Frech, R. "Stretched $PEO-LiCF_3SO_3$ Films: Polarized IR Spectroscopy and X-Ray Diffraction", *Electrochim. Acta* **2007**, in press.

6. Publications Supported under this Grant.

a. Papers published in peer-reviewed journals

   (i) Burba, C. M.; Frech, R. " A Raman and FTIR Spectroscopic Study of Li_xFePO_4 ($0 \le x \le 1$)", *J. Electrochem. Soc.* **2004**, *151(7)*, A1032-A1038.

   (ii) Burba, C. M.; Frech, R. "Electrochemical, Spectroscopic, and Thermal Investigations of $LiSn_2(PO_4)_3$ and $Sn_3(PO_4)_2$ Anodes During the First Discharge", *J. Electrochem. Soc. 152(6)*, **2005**, A1233-A1240.

   (iii) Burba, C. M.; Frech, R. "Spectroscopic Measurements of Ionic Association in Solutions of $LiPF_6$", *J. Phys. Chem. B* **2005**, *109*, 15161-15164.

   (iv) Burba, C. M.; Frech, R., "Modified Coin Cells for *In Situ* Raman Spectroelectrochemical Measurements of Rechargeable Lithium Batteries", *Appl. Spec.* **2006**, 60(5), 490-493.

   (v) Burba, C. M.; Frech, R. "Vibrational Spectroscopic Investigation of Structurally-Related $LiFePO_4$, $NaFePO_4$, and $FePO_4$ Compounds", *Spectrochim. Acta A.* **2006,** 65(1), 44-50.

   (vi) Burba, C. M.; Frech, R. "Vibrational Spectroscopic Study of Lithium Intercalation into $LiTi_2(PO_4)_3$", *Solid State Ionics*, **2006,** *177(17-18)*, 1489-1494.

   (vii) Burba, C. M.; Frech, R. "*In Situ* Transmission FTIR Spectroelectrochemistry: A New Technique for Studying Lithium Batteries", Electrochim. Acta **2006**, *52*, 780-785.

   (viii) Burba; C. M.; Frech, R. "Vibrational Spectroscopic Studies of Monoclinic and Rhombohedral $Li_3V_2(PO_4)_3$", *Solid State Ionics,* **2007**, 177, 3445-3454.

b. Papers published in non-peer-reviewed journals or in conference proceedings
   None
c. Papers presented at meetings, but not published in conference proceedings.

(i) C. Burba and R. Frech, "An Infrared Spectroscopic Study on the Reaction of Lithium with Lithium Tin(IV) Phosphate and Tin(II) Phosphate", 205th Meeting of The Electrochemical Society, San Antonio, TX, May 9-13, 2004.

(ii) C. Burba and R. Frech, "Vibrational Spectroscopic Investigation of Li Extraction from Monoclinic and Rhombohedral $Li_3V_2(PO_4)_3$", Symposium D1, "Intercalation Compounds for Battery Materials", 205th Meeting of The Electrochemical Society Honolulu, HI, October 3- 8, 2004.

(iii) C. Burba and R. Frech, "Does $LiPF_6$ Form Ion-Pairs in Aprotic Solvents?" 60th Southwest Regional Meeting of the American Chemical Society, Fort Worth, TX, Sept. 29 – Oct. 2, 2004. (Poster).

(iv) R. Frech and C. M. Burba, "Stretched $PEO-LiCF_3SO_3$ Films: Polarized IR Spectroscopy and X-Ray Diffraction", 10th International Symposium on Solid Polymer Electrolytes, Foz do Iguacu, Brazil, October 15-19, 2006. (Invited paper).

d. Manuscripts submitted but not published

(i) Burba; C. M.; Frech, R. "Stretched $PEO-LiCF_3SO_3$ Films: Polarized IR Spectroscopy and X-Ray Diffraction", *Electrochim. Acta* **2007,** in press.

(ii) Burba; C. M.; Frech, R. "Local Structure in the Li-Ion Battery Cathode Material $Li_x(Mn_yFe_{1-y})PO_4$ for 0 < x < 1 and y = 0.0, 0.5, and 1.0", *J. Power Sources*, submitted.

e. Technical reports submitted to ARO

Year 1 Interim Report

Year 2 Interim Report

Year 3 Interim Report

7. List of all participating scientific personnel showing any advanced degrees earned by them while employed on the project:

Christopher M. Burba; Ph.D. degree awarded Spring, 2006.

8. Report of Inventions

None

9. Bibliography

(1) Andersson, A. A.; Kalska, B.; Haggstrom, L.; Thomas, J. O. *Solid State Ionics* **2000**, *130*, 41.

(2) Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B. *J. Electrochem. Soc.* **1997**, *144*, 1188.

(3) Burba, C. M.; Frech, R. *J. Electrochem. Soc.* **2003**, *accepted for publication subject to revision.*

(4) Frech, R.; Zhang, X. *Electrochim. Acta* **1997**, *42*, 475.

(5) Apella, M. C.; Baran, E. J.; Etcheverry, S. B.; Mercader, R. C. *Monatsch. Chem.* **1983**, *114*, 1149.

(6) Behm, M.; Irvine, J. T. S. *Electrochim. Acta* **2002**, *47*, 1727.

(7) Morcrette, M.; Leriche, J.-B.; Patoux, S.; Wurm, C.; Masquelier, C. *Electrochem. Solid-State Lett.* **2003**, *6*, A80.

(8) Lin, S.-C.; Grondey, H.; Strobel, P.; Anne, M.; Nazar, L. F. *J. Am. Chem. Soc.* **2003**, *125*, 10402.

(9) Barj, M.; Perthuis, H.; Colomban, P. *Solid State Ionics* **1983**, *11*, 157.

(10) Yin, S.-C.; Grondey, H.; Strobel, P.; Anne, M.; Nazar, L. F. *J. Am. Chem. Soc.* **2003**, *125*, 10402.

(11) Paroux, S.; Masquelier, C. *Chem.Mater.* **2002**, *14*, 5057.

(12) Tarte, P.; Rulmont, A.; Liegeois-Duykaerts, M.; cahay, R.; Winand, J. M. *Solid State Ionics* **1990**, *42*, 177.

(13) Doeff, M.; Hu, Y.; McLarnon, F.; Kostecki, R. *Electrochem. Solid-State Lett.* **2003**, *6*, A207.